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(54) PRODUCTION OF RESILIENT FIBER OF PROPYLENE POLYMER

(70) Newton, Richard C. and Buchanan, David R., Greenville, South Carolina, U.S.A.

Granted to Phillips Petroleum Company, Bartlesville, Oklahoma, U.S.A.

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PRODUCTION OF RESILIENT FIBER OF PROPYLENE POLYMER

It is common practice in the textile industry to utilize thermal and/or mechanical treatment of fibrous materials to improve the characteristics thereof for a particular application. For instance, heat treatment for a period of 5 seconds to 5 minutes is disclosed in Bierhaum et al, U.S. 3,413,397, to impart a "set" to synthetic filaments. Indeed, it has long been known to anneal synthetic polymeric material in an air oven for a period of time in the range of one-half hour to one hour so as to reorder the crystal structure.

It has been found that conventional air oven annealing results in an improvement in resilience of fibers. However, with polypropylene, such oven annealing results in a serious deterioration in soiling characteristics.

It is an object of this invention to provide a process for producing soil resistant resilient fiber of propylene polymer; it is a further object of this invention to reorder the crystal structure of propylene polymer by rapid heating for a short period of time without creating a tendency to soil; and it is yet a further object of this invention to provide resilient soil resistant fibers of propylene polymer.

In accordance with this invention, fibers of a propylene polymer are treated with saturated steam for 0.01 to 2 seconds while maintaining tension on said fibers.

It is essential to the invention that the contact time in the treating zone be no more than 2 seconds, generally within the range of 0.01 to 2, preferably 0.4 to 0.6 seconds. It is preferred that saturated steam be used as a treating agent as opposed to super heated steam.

A rapid heating rate is desirable and, in fact necessary, to obtain the maximum effect of crystal length enhancement. The mechanism believed to be responsible for crystal growth involves local melting of zones of crystal imperfection and reorganization of the molecules involved to increase the size of existing highly crystalline zones, the desired effect, or to form small crystals of themselves with no increase in crystal length or resilience. The former reaction is favored by higher temperatures and rapid annealing rates. Rapid annealing rates are also needed because polypropylene resins

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contain small amounts of material which tends to exude to the surface upon prolonged heating (several minutes or more) at temperatures high enough to get improved resilience. This material on the surface of the fiber makes it unaccpetable for use in carpets because it causes a serious soiling problem.

Because of the rapid movement of filament tow necessary to achieve the short contact time, the steam treating zone is preferably completely open at each end and of such cross sectional size that the tow, which expands on contact with the steam, substantially completely fills the zone. Thus, the pressure of the steam at the actual moment of contact may vary somewhat and will in all events be lower than the pressure prior to introduction into said zone. Surprisingly, however, it has been found that improved results are obtained if the steam is under pressure of 55 to 90, preferably 70 to 80 psig, prior to introduction into contact with the filament tow.

Preferably, tension is maintained on the filament during the treating step although the tension does not have to be controlled so as to maintain the filaments being treated at exactly their initial length. Generally, the tension will be such that the final length of a filament passing through said steam treating zone will be 80-100, preferably 90-100%, of its original length. However, this is not a limitation to the process; yarn with high crystal length, high plug height recovery and good resilience has been produced with shrinkage during treatment requiring from 0 to 30%. This invention allows effective treatment of large denier tow at line speeds of 100 to 250, preferably 125 to 150, meters per minute.

Steam temperature and pressure and also the time should be correlated so that no substantial melting of the filaments results. Generally, the filaments will be heated to a temperature of 10°C to 35°C below the melting point of the polymer constituting same. For polypropylene homopolymer the preferred temperatures to which the yarn is heated is in the range of 135°C to 160°C.

The resulting fibers have improved resilience due to a reordering of the crystal structure. This change can be characterized by small angle X-ray diffraction. Resilient fibers have been found to exhibit relatively intense

small angle X-ray diffraction in the fiber axis direction with maximum diffracted intensity at an angle $2\theta_m$ such that the calculated long period "d" is increased, generally to at least 160Å, and the calculated crystal length is increased to within the range of 125 to 200Å, preferably 140 to 160Å. Very little further improvement in resilience is obtained after the crystal length reaches 170Å and additional heating to further increase the crystal length results in the beginning of deterioration in the soiling characteristics. These crystal lengths compare with the initial crystals which are of imperfect structure and less than 110Å, generally 85 to 100Å in length.

X-ray diffraction measurements on polypropylene fibers annealed by this process show the following molecular structural characteristics:

A. Increased long period, i.e. crystal length over 140Å.

B. Decreased breadth of the maximum in small-angle scattering.

C. Increased intensity of small angle scattering.

D. Little or no increase in crystal orientation.

E. No increase in "gamma" orientation.

Also there is little change in most fiber mechanical properties, i.e. tenacity, elongation, modulus. Dye receptivity however is greatly improved by the steam treatment in accordance with the invention.

The same crystal size and general structural characteristics can be obtained by heating the fiber in an air oven for 30 minutes to an hour at a temperature in the case of polypropylene of about 150°C. However, the resulting fiber has greatly deteriorated resistance to soiling.

The techniques of this invention are suitable for treatment of any propylene polymer or copolymer wherein propylene is the major constituent or with blends of polypropylene and other materials wherein polypropylene is the major constituent. Preferably, however, the fiber is a polypropylene homopolymer or at most a copolymer containing no more than 3% of a second monomer. Of course, conventional additives such as antioxidants, UV stabilizers, fillers, pigments, delustering aids, dye acceptors, antistatic agents, and the like may be present in the composition.

While the description hereinabove has referred to fibers or filaments as a practical matter treatment will usually be carried out on a filament tow comprising a large number of individual fibers or filaments.

The steam treating zone can comprise any means for exposing the fibers to a large volume of steam in a short period of time. One means is to heat the fibers to the desired temperature by passing the fibers through a fluid jet. Such jets are well known in the art and will not be described herein. Preferably, however, the zone will comprise an elongated oval chamber open at each end within a jacket, and will be utilized with relatively large denier tow which will expand to fill essentially the entire volume of the treating zone. For example, the invention is of particular utility in treating tow of greater than 100,000, preferably 250,000-750,000 denier. The oval chamber can have a ratio of the major axis to minor axis of 2:1 to 200:1, preferably 25:1 to 200:1. Thus, the tow will have a like width to height ratio on expanding after contact with the steam.

In the drawings forming a part hereof wherein like reference characters denote like parts in the various views, FIGURE 1 is a side view partially in section of an apparatus in accordance with the invention; FIGURE 2 is a cross-section along lines 2-2 of FIGURE 1; FIGURE 3 is a longitudinal section along lines 3-3 of FIGURE 1; and FIGURE 4 is a cross-section of an apparatus in accordance with an alternative embodiment of the invention.

Referring now to the FIGURES, particularly FIGURE 1, there is shown an apparatus for conditioning tow in accordance with the invention. A continuous length of tow 10 is fed through a first tensioning means comprising rollers 12, 14 and 16, which in combination with a second tensioning means made up of rollers 18, 20, and 22, serve as a tensioning means to maintain tension on the yarn as it passes through a treating zone. Specifically, the fiber passes through oval chamber 24 which has a flared forward end 26, chamber 4 has a second open end 29. Surrounding oval tube 24 is jacket 30 which is sealed around each end thereof to oval chamber 24. Jacket 30 contains

steam introduction means 32. The steam exhausts at both end 26 and with the tow at end 28. As can be seen from FIGURE 2, chamber 24 has an oval cross-section with opposed generally flat walls 36 at each end of a major axis thereof and generally flat walls 38 at opposite ends of a minor axis thereof.

Referring now to FIGURE 3, there is shown a longitudinal section of jacket 30 showing holes 40 and oval chamber 24. It is preferred that two holes not be placed directly across from each other. One convenient pattern is to place the holes in a spiral pattern, each successive hole being rotated 90° and spaced forward axially a short distance. The size of the holes can vary greatly generally being within the range of 10-200, preferably 15 to 50 mils in diameter. Another preferred pattern is a randomized placement of the holes.

As can be seen from FIGURE 1, steam enters through inlets 32 and into the annular space between jacket 30 and oval chamber 24 and thence through holes 40 into contact with yarn 10. This contact of steam with yarn 10 causes the yarn to fluff out as can be seen from FIGURE 1 to substantially fill the space with chamber 24.

FIGURE 4 shows a preferred embodiment wherein the elongated oval treating chamber is made by welding flat plates having holes therein to a split pipe and affixing the two halves together with spacers. The inner surfaces of the spacers form flat side walls 36a of the oval treating chamber with the portion of the flat plates between the spacers forming flat side walls 38a. The two halves of the pipe form jackets 30a with steam introduction means 32a.

While the steam jacket 30 is shown round in FIGURES 1-3 and is shown formed from round pipe in FIGURE 4, it can be any convenient shape such as square and the like.

EXAMPLE I

Melt spun yellow pigmented polypropylene fibers from a creel containing a plurality of yarn packages were plied together through ring guides to form a tow band of about 500,000 denier. The polypropylene had a melting point of

about 170°C. The tow, maintained under tension, was passed through two sets of rolls allowing no more than about 10 percent relaxation. The apparatus of this invention was placed between these rolls. The tow was then passed to a stuffer-crimper and cut into staple. The treating apparatus of this invention was six feet long overall and had an oval treating chamber with a 32 to 1 aspect ratio and an effective treating length of 58 inches. The oval treating chamber was 4 inches wide by 1/8 inch deep with 660 1/32 inch diameter holes on a 3/8 by 2 inch grid on the flat sides (the spacing on the two plates was offset slightly so holes did not occur directly across from each other). The shell was made from a split 4-inch diameter pipe with 1/8-inch polytetrafluoroethylene gaskets so as to form separate steam chambers around each flat side as shown in FIGURE 4. Each steam enclosure had two 1-inch steam inlets. Saturated steam was used as the treating fluid at a temperature of 157°C and a pressure of 75 psig. Residence time for treating tow in the apparatus was 0.5 seconds. Both treated and untreated samples were made. Samples were cut into staple 1-1/2 inches long. One gram samples were taken from the prepared staple and hand carded. The samples were placed in a 1-inch diameter die and compressed at 10,000 psi for one minute. Measurements of returned plug height were taken after 30 seconds and 24 hours. Crystal lengths of both samples were measured by small angle X-ray diffraction. The treated samples had a longer crystal length and exhibited a higher degree of resilience by plug height measurement as shown in Table 1 and was a satisfactory product for carpet yarn.

Table 1

Sample	Denier Per Fiber (Nominal)	Crystal Length	Plug Height (24 hrs.)
Control (untreated)	18	105 Å	0.244 inches
Run 1 (treated)	18	155.8 Å	0.636 inches

Large denier tow was annealed in an air oven under optimum conditions to improve resiliency. The resulting product was not satisfactory for carpet yarn.

EXAMPLE II

Five-ply, yellow-pigmented untextured yarn of about 5,000 denier was treated in a small scale apparatus similar to that described in Example I. The inner tube had an active treating length of 1 meter and was made from 1/8 inch .035 inch wall stainless steel tubing with 30 1/64 inch diameter holes on a 1-23/64 inch spacing. The outer tube was 1/2 inch diameter stainless steel tubing sealed at both ends against the inner tube, with one 1/4 inch inlet for steam. The yarn was treated with saturated steam at 75 psig. The yarn was passed through the apparatus at 100 meters per minute, having a residence time of 0.6 seconds. Crystal length of the fibers were measured by small angle X-ray and found to be 160Å. For comparison purposes, additional samples of an untreated control yarn and a second sample annealed in an oven at 155°C for one hour. The three samples were made into level loop staple carpets and subjected to walk-on tests. The treated carpet exhibited improved resilience over both samples and improved soil resistance over the oven-treated yarn as shown in Table II.

Table II

Sample	Treatment	% Retention of Original Thickness After 19,875 Steps	Unsoiled (%R)*	Floor Soiling (Δ % R)
Control 2	Untreated	76	74.6	24.1
Control 3	Oven 155°C 1 hr.	79.8	70.1	38.3
Run 2	Steam tube 0.5 sec.	80	75.6	27.8

*%R - Reflectance as measured by the Color Eye at 600 mu; the extent of soiling is indicated by the magnitude of the change in reflectance, Δ% R.

While this invention has been described in detail for the purpose of illustration, it is not to be construed as limited thereby but is intended to cover all changes and modifications within the spirit and scope thereof.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method for treating fibers of polypropylene, copolymers wherein propylene is the major constituent or blends where polypropylene is the major constituent to effect improved resistance to soiling and improved resilience comprising: contacting said fibers with saturated steam for a time within the range of 0.01 to 2 seconds whereby said fibers reach a temperature of 135°C to 160°C while maintaining tension on said fiber.

2. A method according to claim 1 wherein said steam is injected directly onto said fiber from a source under a pressure of 55 to 90 psig.

3. A method according to claim 1 wherein said contact time is 0.4 to 0.6 seconds.

4. A method according to claim 3 wherein said fibers are made of propylene homopolymer.

5. A method according to claim 4 wherein said fiber is in the form of a filament tow having a denier of greater than 100,000 and said contacting occurs by passing said tow axially through an elongated oval zone of such size that on contact with said steam said tow expands to substantially fill said zone and is thus shaped to a width to height ratio within the range of 25:1 to 200:1.

6. A soil resistant fiber of propylene polymer having a crystal length as determined by X-ray diffraction of 125-200Å.

7. An article according to claim 6 wherein said polymer of propylene is a propylene homopolymer.

8. An article according to claim 7 wherein said crystal length is within the range of 140-160Å.

9. An article according to claim 8 in the form of carpet pile.

10. An article according to claim 9 wherein said fiber further exhibits a long period, d, of at least 160Å as measured by X-ray diffraction.

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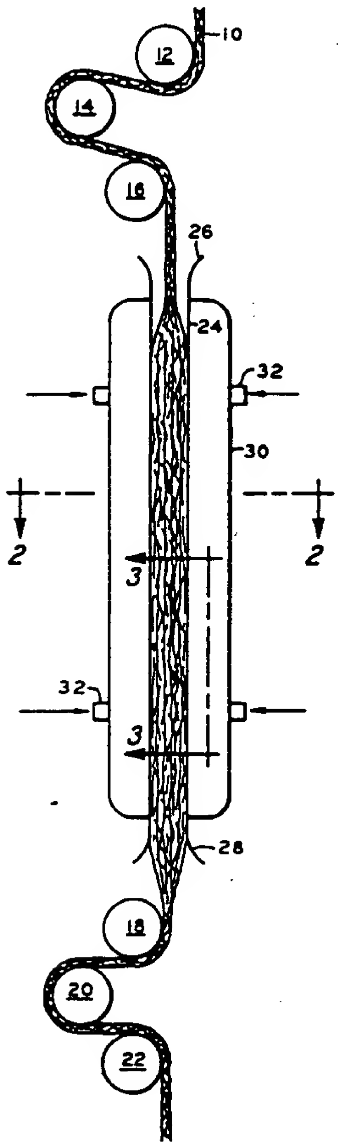

FIG. 1

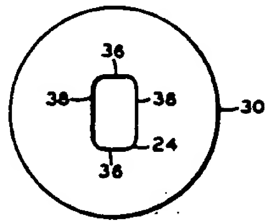

FIG. 2

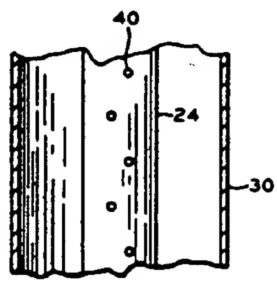

FIG. 3

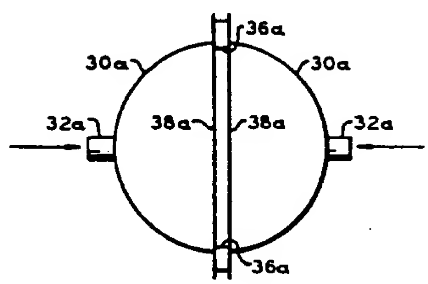

FIG. 4